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Direct observation of hindered eccentric rotation of an individual molecule: Cu-phthalocyanine on C₆₀

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Individual Cu-phthalocyanine molecules have been investigated by scanning tunnel microscopy on a closed packed film of C₆₀ at various temperatures. The molecules are found to bind asymmetrically to one C₆₀. While they remain in one position at low temperature, they can hop between six equivalent positions at higher temperatures performing a hindered eccentric rotation around the binding C₆₀ molecule. At room temperature only the time average over different positions is observed.

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The fascinating capability of scanning tunneling microscopy to image individual molecules has been first demonstrated for isolated molecules of copper phthalocyanine (CuPc) by Gimzewski, Stoll, and Schlittler¹ and by Lippel *et al.*² Although the technique primarily provides information about the static surface structure, there are impressive examples how it may be used to analyze the dynamics of molecules at surfaces in a way that is complementary to techniques of electron-stimulated desorption ion angular distribution as described, e.g., by Yates *et al.*³ The diffusion of single atoms and molecules has been observed, e.g., for Pb on Ge(111),⁴ benzene on Cu(111),⁵ and Si dimers on Si(001).⁶ The rotation of individual molecules between stable positions has been observed by scanning tunnel microscopy (STM) by looking at the same molecule at subsequent times. Mo (Ref. 7) could demonstrate that dimers of antimony on a Si(001) surface may hop between two orthogonal positions upon excitation by increased bias voltage. Stipe, Rezaei, and Ho⁸ could not only visualize the O₂ molecule on Pt(111) in three positions rotated relative to each other by 120°, but could also identify the jump into a particular site by analysis of the tunneling current. The observation of the continuous rotation of an individual molecule was reported by Gimzewski *et al.*,⁹ who found that only the time average is apparent in the STM topography. This is readily understood since the scan frequency is orders of magnitude slower than the rotational frequency. For the particular molecule this leads to a ring-shaped structure. Hersam, Guisinger, and Lyding¹⁰ observed a similar structure due to the eccentric rotation of CuPc on Si(001). Stipe, Rezaei, and Ho were able to analyze the vibration¹¹ and the coupling of vibrational and rotational modes¹² for acetylene on Cu(100) by means of tunneling spectroscopy at low temperature. A bimolecular system that resembles the one chosen in this paper has been investigated by Cuberes, Schlittler, and Gimzewski¹³ who demonstrated the molecular manipulation of individual C₆₀ molecules deposited on a monolayer of 4,4'-dimethylbianthrone preadsorbed on Cu(111).

In the present paper, we report on the first observation of a time average of a hindered rotation of an isolated molecule. The CuPc molecule has by its chemical structure a fourfold symmetry that has been observed experimentally by electron

microscopy and various studies by STM. However, for the given system STM images taken at room temperature show a ring with sixfold symmetry and a diameter substantially larger than the one of the molecule. When decreasing the temperature the images of the rings become unstable and finally at 50 K only images of a CuPc molecule of expected size locked in an asymmetric position are found.

The experiments were carried out by a slightly modified commercial variable temperature STM (Omicron). The sample temperature can be adjusted by a liquid-helium flow cryostat and by electrical heating. It allows the investigation in a temperature range between 50 and 600 K. For the given experiment it was only used at room and at low temperature. The tunneling tips have been prepared by electrochemical etching of a tungsten wire. The tips have been further processed *in situ* by sputtering with Ar⁺ ions and by field emission, shortly before the experiment.

The samples have been prepared in several steps. First a (111) oriented gold film has been epitaxially grown on a mica substrate heated to 600 K as described, e.g., in Ref. 14.

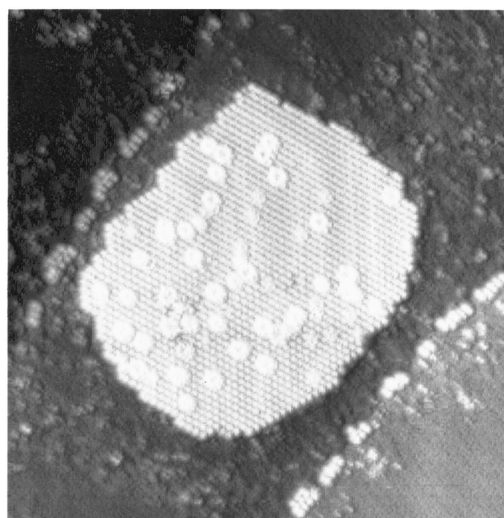


FIG. 1. Overview over a mixed layer of CuPc and C₆₀ at 300 K, the area is 65×65 nm², the tunneling current is 8 pA at 2 V tip bias; the STM data have been partially shaded to enhance the visibility of small details.

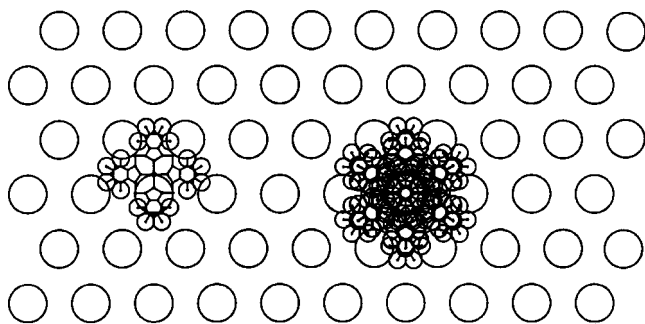


FIG. 2. Schematic drawing of possible positions of the CuPc molecule on C_{60} ; the left side shows an expected stable position that seems to be energetically favorable, the right side displays the corresponding superposition of the six symmetrically equivalent positions.

The mixed layers of CuPc and C_{60} have been prepared either by depositing the C_{60} prior to the CuPc or by the inverse sequence. Surprisingly both methods lead to nearly the same findings. The following description applies to the first case. The equivalent of somewhat less than one monolayer of C_{60} has been deposited by thermal evaporation. These films have been annealed using a linear temperature increase of 1 K/s ending at 600 K. This mainly yields an ordered monolayer of C_{60} . In a final step a fraction of a monolayer of CuPc molecules has been deposited. Again the samples have been annealed, this time to 500 K. As found later the last annealing step is not necessary. The STM images were acquired at low tunneling currents in the range of 3 to 50 pA. The sample bias voltage has been varied in the range from -2.5 V to $+2.5$ V.

Mixed layers of CuPc and C_{60} on Au(111) typically exhibit ordered domains of both molecules. Within the domains the structure is identical to the one that is observed if only one species is present. A mixed phase within one layer has not been observed. Figure 1 displays a typical area of about

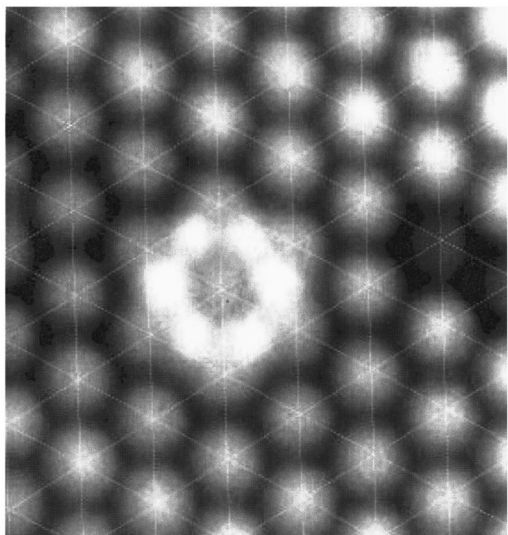


FIG. 3. Individual CuPc molecule on C_{60} ; the area is 6×8 nm², the tunneling current is 3 pA at 1.9 V tip bias.

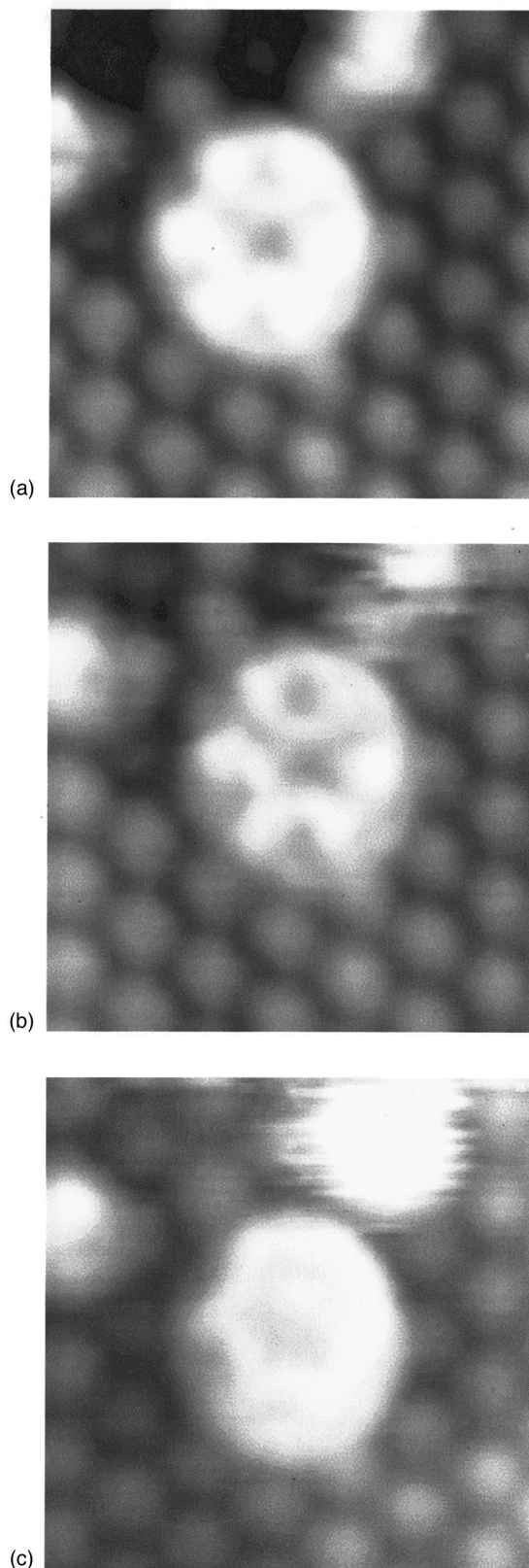


FIG. 4. CuPc on C_{60} measured with a different tunneling tip at 300 K, the area is 6×6 nm² (a) tunneling current of 8 pA at $+1.5$ V tip bias. (b) Tunneling current of 50 pA at $+1.5$ V tip bias. (c) Tunneling current of 50 pA at -1.5 V tip bias.

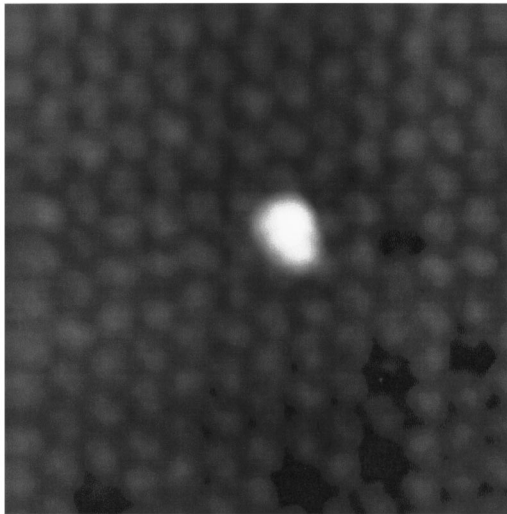


FIG. 5. Individual CuPc molecule at about 50 K; the area is $22 \times 22 \text{ nm}^2$, the tunneling current is 13 pA at -2 V tip bias.

$65 \times 65 \text{ nm}^2$. At the lower right a domain of CuPc is visible. It shows the quadratic ordering discussed by Fritz *et al.*¹⁵ Its domain boundaries are decorated by C_{60} molecules. In the middle of the figure an array of C_{60} molecules can be seen that displays the well-known hexagonal closed packed structure.¹⁶ Between the domains irregular arrangements of mainly CuPc are observed that are typically not stable at room temperature. The subjects of the present paper are the individual CuPc molecules that are found on top of the C_{60} layer. Although the apparent height corresponds well to the expectations for CuPc the observed structure is very surprising. The diameter of the rings amounts to approximately 2.5 nm, which is too large for a single CuPc molecule (about 1.2 nm in diameter), even if one considers that the lateral dimension of a protrusion is always overestimated by a scanning probe microscope. Furthermore, the ring structure clearly exhibits a sixfold symmetry that seems to contradict to the fourfold symmetry of the CuPc molecule. However, rings of this type are only found if CuPc was present and have not been observed on pure C_{60} films. The latter sometimes exhibit defects in form of rings that, however, are much smaller in height and lateral dimensions as found by Altman and Colton.¹⁶

To explain the observed feature a possible position of the CuPc molecule on the C_{60} layer is shown in a schematic drawing in Fig. 2. At first one might expect a configuration where the CuPc is placed symmetrically on top of a C_{60} molecule. However, this does not allow for a favorable position of the four lobes of the CuPc. A more plausible stable position is displayed on the left side of Fig. 2. One of the five-membered rings of the CuPc formed by four carbon atoms and one nitrogen atom sits on top of the C_{60} . That permits the three remaining lobes to squeeze in between the neighboring C_{60} molecules. However, at room temperature a rotation of the molecule is quite likely. According to the symmetry of the C_{60} layer six equivalent positions are possible that are obtained by rotation by multiples of 60° around the “anchoring” C_{60} molecule. The right side of Fig. 2 shows

the superposition of these configurations. It shows a striking similarity to the observed rings as displayed in Fig. 1 and 3.

Figure 3 shows a small area of $6 \times 8 \text{ nm}^2$ with a single CuPc molecule in the center. The dashed white lines indicate the hexagonal order of the C_{60} layer. Each intersection marks a center of a C_{60} molecule. It clearly shows that the six maxima of the ring are located between the C_{60} as in the right drawing of Fig. 2.

The fact that the ring is not continuous shows that the molecule is not permanently rotating but hops between possible positions. If one assumes a potential barrier of 150 meV (Ref. 17) between the positions, the jump frequency is at room temperature so high that a single jump is not resolved within the band width of the current preamplifier for the tunneling current. Furthermore, the STM images only show the time average over the possible positions. Since a change of the central C_{60} molecule is not observed, the binding to the C_{60} molecule at the center of the ring is significantly stronger. The proposed hindered rotation is also consistent with the eccentric motion of the molecule, which could not be explained for the case of a continuous rotation.

It is generally assumed that at room temperature the C_{60} molecules may rotate on Au(111). Hence, the discussed motion of the CuPc molecule may be facilitated by the rotation of the underlying C_{60} molecules that may act as in a nanoscopic “ball bearing.”

The observed ring of the rotating CuPc molecule shows some variation depending on the tunneling tip and the tunneling parameters. Figures 4(a)–(c) show representative results of a series of measurements performed varying the tunneling bias between -2.5 and $+2.5 \text{ V}$, and the tunneling current between 3 and 50 pA. The data have been taken in another experimental run with a different tunneling tip to that in Fig. 3. From the defects, e.g., to the upper right surrounding the molecule it can be clearly seen that the images show the same molecule. Figure 4(a) has been acquired at a low tunneling current of 8 pA and a bias voltage of 1.5 V at the tip. Figure 4(b) displays the corresponding image at the same bias but a larger tunneling current of 50 pA. Since there is no significant variation between the two images, it may be concluded that the observation is not due to a process that is driven by the tunneling current, e.g., that the rotation is induced. If the bias polarity is changed to -1.5 V at the tip the structure appears somewhat blurred but the principal features remain. It is, thereby, excluded that the observation is due to a specific electronic resonance that should be limited to a small range of bias voltages.

An important prediction of the proposed model is that the ring structure should disappear at low temperatures. In fact it has been observed that at a temperature of about 150 K the tunneling current becomes noisy when the tunneling tip is placed on the ring structures. At temperatures below approximately 80 K finally the molecules are locked in one position as sketched on the left side of Fig. 2. The observed topography of a single molecule at 50 K is shown in Fig. 5. Now the size of the protrusion corresponds well to the size of the molecule. It clearly exhibits an asymmetry as one would expect according to Fig. 2.

To summarize, for the example of CuPc on C_{60} , we have observed the hindered eccentric rotation of individual molecules. If the temperature is high enough the molecules may hop between the different positions at high frequency. In the

topography obtained by scanning tunneling microscopy only the time average is observed yielding a ring structure with six maxima. At low temperatures the molecules become locked in one position.

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¹⁷A rough estimate for the activation energy is obtained by a fit to the Arrhenius equation using that there is no hopping at 50 K, a tunneling current noise with a typical frequency of about 500 Hz at 150 K and a hopping rate larger than 105 Hz at room temperature.